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Pretreatment liquor for preparing textile substrates for inkjet printing

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The present invention relates to aqueous pretreatment liquors for preparing textile substrates for inkjet printing.

- 10 It is known to treat textile materials which are to be printed by the inkjet printing process with a pretreatment liquor to improve the performance properties of the printed textiles. This pretreatment is intended to improve the holdout of the inks on the textile substrate, and to provide a higher color strength and also better fixation of the inks on the substrate. It would be desirable to have distinctly crisper contours (improved definition) for the prints
- 15 on the substrate in order that higher resolutions (higher dpi) may be achieved for the prints.

Prints with pigment inks can in principle be carried out on all textile fabrics. Numerous patent applications describe the use of cationic substances or thickeners to improve the ink holdout when inkjet printing with reactive dyes on cotton or other cellulosic fibers.

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EP-A 0 928 841 describes the use of natural thickeners and of divalent metal salts when printing direct dyes and pigments onto silk. Polyquaternary or polycationic compounds are not mentioned, nor are disperse dyes.

- 25 WO 99/33669 discloses the preprint treatment of a textile with cationic compounds to improve the holdout of disperse dye inks. Only low molecular weight cationic compounds are mentioned, no polyquaternary or polycationic compounds.

- 30 US 6,001,137 describes the use of polycationic compounds based on epichlorohydrin copolymers for improving fixation. Improved ink holdout is not mentioned.

- WO 00/03081 describes a pretreatment of textiles with textile binders and melamine crosslinkers for inkjet printing with pigments. The pretreatment results in good fastnesses for the prints. There is no mention of an improved printed image due to superior ink
- 35 holdout and the use of cationic compounds.

JP 62231787 describes the use of divalent inorganic metal salts and/or cationic compounds and crosslinkers for preparing textiles for inkjet printing with pigments. The crosslinker leads to crosslinking with a binder included in the ink. The use of polycationic compounds is not mentioned, nor is the use of polyethylene glycol derivatives or other thickeners.

WO 00/56972 describes the use of cationic polymers and copolymers and also of polymer latices as binders for the pretreatment of textile substrates for inkjet printing.

The disadvantage with prior art processes is a frequently inadequate definition of the printed image on the textile substrate. This is due to the spreading of the inks on the substrate.

It is an object of the present invention to provide a pretreatment liquor for preparing textile substrates for inkjet printing which produces improved ink holdout on the printed textile substrates. It is a particular object of the present invention to improve the ink holdout of cellulosic textile substrates printed with pigment inks and of textile polyester fiber substrates printed with disperse dye inks. It is a further object of the present invention to improve the fixation for printing with disperse dye inks and so achieve an enhanced brilliance and color strength for the prints.

We have found that these objects are achieved by an aqueous pretreatment liquor for preparing a textile substrate for inkjet printing, comprising

- (A) one or more polycationic compounds,
- (B) one or more thickeners,
- (C) optionally customary additives,
- (D) water.

Component (A) in the aqueous pretreatment liquors according to the present invention is one or more polycationic compounds.

Useful polycationic compounds include for example cationic homopolymers or copolymers of diallyldialkylammonium monomers, such as diallyldimethylammonium chloride, cationic acrylates and acrylamides such as acryloyloxyethyltrimethylammonium chloride or acrylamidoethyltrimethylammonium chloride, quaternary vinylpyridines such as methylvinylpyridine chloride, polyalkylamine polymers and copolymers, also

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polyallylamine hydrochloride, allylamine hydrochloride-diallylamine hydrochloride copolymer, N-vinylacryloylamidine hydrochloride-acrylamide copolymer, dialkylamine-epichlorohydrin polymer, polyamide-polyamine-epichlorohydrin polymer, dicyandiamide-formaldehyde polycondensate, polyethylenepolyamine-dicyandiamide polycondensate, polyethyleneimine hydrochloride, poly(meth)acryloyloxyalkyldialkylamine hydrochloride, (meth)acryloyloxyalkyldialkylamine hydrochloride-acrylamide copolymer and poly(meth)acryloyloxyalkyltrialkylammonium chloride.

Preferred polycationic compounds (A) are homo- or copolymers of diallyldialkylammonium monomers, such as polydiallyldimethylammonium chloride (polyDADMAC), polydiallyldiethylammonium chloride (polyDADEAC), polydiallyldimethylammonium bromides (polyDADMABs), polydiallyldiethylammonium bromide (polyDADEAB), particular preference is given to polymers or copolymers of diallyldimethylammonium chloride and especial preference is given to diallyldimethylammonium chloride homopolymer (polyDADMAC).

Copolymers of the monomers mentioned may also contain nonionic monomers, for example vinylpyrrolidone, (partially saponified) vinyl acetate or hydroxy(meth)acrylate, as comonomers.

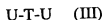
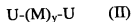
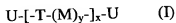
Processes for preparing diallyldialkylammonium homo- or copolymers are described for example in US 4,742,134, US 5,283,306 and EP-A 0 264 710.

In one embodiment of the present invention, the aqueous pretreatment liquors comprise polymers or copolymers of diallyldialkylammonium monomers, preferably polymers or copolymers of diallyldimethylammonium chloride and more preferably diallyldimethylammonium chloride homopolymer, as polycationic compounds (A), and one or more thickeners (B).

Component (B) in the aqueous pretreatment liquors according to the present invention is one or more thickeners.

Useful thickeners (B) include natural thickeners such as alginates, polysaccharides, starch, carboxymethylcellulose, guar gum powder and also derivatives thereof, and synthetic thickeners such as optionally acrylic acid homo- and copolymers.

Preferred thickeners (B) are associative thickeners of the general formula (I), (II) and/or (III)



10 where:

(M)_y is a unit derived from polyalkylene ether, M being an individual alkylene ether unit and y being from 1 to 100 000, and preferably from 10 to 10 000,

T is in each occurrence the same or different unit derived from a diisocyanate,

x is on average from 1 to 500, preferably from 1 to 2 and more preferably about 1.

15 U is in each occurrence the same or different unit of at least 4 carbon atoms and preferably at least 6 carbon atoms, that is derived from aliphatic or aromatic alcohols, alkoxyated alcohols, thiols, amines or carboxylic acids.

20 In one embodiment of the present invention, the aqueous pretreatment liquors comprise one or more polycationic compounds (A) and one or more associative thickeners of the general formula (I) and/or (II).

Associative thickeners of the general formula (I) are obtainable by reaction of

- 25 (i) polyetherdiols,
 (ii) diisocyanates and
 (iii) compounds, R of the general formula R-OH, R-SH, R-NH₂, RR'NH or R-COOH, where R is a hydrophobic aliphatic or aromatic radical of at least 4 carbon atoms and R-OH may have been alkoxyated, and also further derivatives thereof that are
 30 capable of forming a urethane, thiourethane or urea bond.

Polyetherdiols (i) for the purposes of the present inventions are polyethylene glycol, polypropylene glycol and polytetrahydrofuran, but also copolymers of ethylene oxide and propylene oxide or butylene oxide or terpolymers of ethylene oxide, propylene oxide and butylene oxide, and the copolymers can be present as block copolymers or random
 35 copolymers or terpolymers.

- Useful diisocyanates (ii) include diisocyanates having NCO groups of the same or a different reactivity. Examples of diisocyanates having NCO groups of the same reactivity are aromatic or aliphatic diisocyanates, preference being given to aliphatic diisocyanates
- 5 such as tetramethylene diisocyanate, hexamethylene diisocyanate (HDI), octamethylene diisocyanate, decamethylene diisocyanate, dodecamethylene diisocyanate, tetradecamethylene diisocyanate, trimethylhexane diisocyanate, tetramethylhexane diisocyanate, 1,4-, 1,3- or 1,2-diisocyanatocyclohexane, 4,4'-diisocyanatocyclohexylmethane, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (isophorone
- 10 diisocyanate) and 2,4- and 2,6-diisocyanato-1-methylcyclohexane, of which hexamethylene diisocyanate and isophorone diisocyanate are particularly preferably preferred. A further particularly preferred diisocyanate is m-tetramethylxylene diisocyanate (TMXDI).
- 15 Preferred diisocyanates having NCO groups of differing reactivity are the readily and inexpensively available isocyanates such as for example 2,4-tolylene diisocyanate (2,4-TDI), 2,4'-diphenylmethane diisocyanate (2,4'-MDI), triisocyanatotoluene as representatives of aromatic diisocyanates or aliphatic diisocyanates, such as 2-butyl-2-ethylpentamethylene diisocyanate, 2-isocyanatopropylcyclohexyl isocyanate, 2,4,4- or
- 20 2,2,4-trimethylhexamethylene diisocyanate, 2,4'-methylenebis(cyclohexyl) diisocyanate and 4-methylcyclohexane 1,3-diisocyanate (H-TDI).

Further examples of isocyanates having groups differing in reactivity are 1,3-phenylene diisocyanate, 1,4-phenylene diisocyanate, 1,5-naphthylene diisocyanate, diphenyl

25 diisocyanate, toluidine diisocyanate and 2,6-tolylene diisocyanate.

It is naturally also possible to use mixtures of two or more of the aforementioned isocyanates.

- 30 Polyisocyanates can be used to a certain extent alongside diisocyanates, for example in amounts of up to 10% by weight based on the total amount of di- and polyisocyanate. Examples of useful polyisocyanates are biurets and allophanates of HDI or TDI.

Very particularly preferred diisocyanates are HDI, IPDI, MDI and TDI.

The ratio of polyetherdiols (i) to diisocyanates (ii) is generally in the range from 0.3:1 to 1:1 and preferably about 0.5:1.

The reaction of the diisocyanates with the polyetherdiols is typically carried out in the presence of a catalyst.

The catalysts are preferably used in an amount from 0.01% to 10% by weight and preferably from 0.05% to 5% by weight. The reaction can be carried out in a solvent, in which case useful solvents include in principle all solvents which react neither with the polyurethane nor with the polyether derivative.

Useful catalysts to speed especially the reaction between the NCO groups of the diisocyanates and the hydroxyl groups of the polyetherdiols are the well-known tertiary amines, for example triethylamine, dimethylcyclohexylamine, N-methylmorpholine, N,N'-dimethylpiperazine, 2-dimethylaminoethoxyethanol, diazabicyclo(2.2.2)octane and the like and also in particular organic metal compounds such as titanate esters, iron compounds such as for example iron(III) acetylacetonate, tin compounds, for example tin diacetate, tin dioctanoate, tin dilaurate or the dialkyl derivatives of tin dialkyl salts of aliphatic carboxylic acids such as dibutyltin diacetate, dibutyltin dilaurate or the like.

The synthesis of the associative thickeners is generally carried out without a solvent or in an aprotic solvent, for example in tetrahydrofuran, diethyl ether, diisopropyl ether, chloroform, dichloromethane, di-n-butyl ether, acetone, N-methylpyrrolidone (NMP), xylene, toluene, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK) or 1,4-dioxane. Preferred reaction temperatures are in the range from -20°C to the boiling point of the solvent used. The reaction is generally carried out under atmospheric pressure, but it may also be carried out in autoclaves at up to 20 bar.

Reacting the NCO-terminated products with aliphatic or aromatic alcohols, thiols, primary or secondary amines or carboxylic acids (ii) converts the reaction products of the components (i) and (ii), which contain free isocyanate groups, into hydrophobicized products.

Suitable are in particular alcohols and primary or secondary amines having

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- C₈-C₄₀-alkyl radicals such as n-octyl, n-nonyl, n-decyl, n-dodecyl, n-hexadecyl or n-eicosyl;

5 - C₆-C₁₄-aryl radicals such as phenyl, α -naphthyl, β -naphthyl, 1-anthracenyl, 2-anthracenyl or 9-anthracenyl or heteroaromatic radicals such as α -pyridyl, β -pyridyl, γ -pyridyl, N-pyrrolyl, β -pyrrolyl, γ -pyrrolyl, porphyrinyl, 2-furanyl, 3-furanyl, 2-thiophenyl, 3-thiophenyl, N-pyrazolyl, N-imidazolyl, N-triazolyl, N-oxazolyl, N-indolyl, N-carbazolyl, 2-benzofuranyl, 2-benzothiophenyl, N-indazolyl, benzotriazolyl, 2-quinolyl, 3-isoquinolyl or α -phenanthrolyl;

10 - C₇-C₁₃-aralkyl and preferably C₇- to C₁₂-phenylalkyl such as benzyl, 1-phenethyl, 2-phenethyl, 1-phenyl-propyl, 2-phenyl-propyl, 3-phenyl-propyl, neophyl (1-methyl-1-phenylethyl), 1-phenyl-butyl, 2-phenyl-butyl, 3-phenyl-butyl and 4-phenyl-butyl, more preferably benzyl.

15 The alcohols R-OH can also have been alkoxyated with ethylene oxide, propylene oxide or butylene oxide, in which case not only homo- but also block copolymers of the alkylene oxides mentioned can be used, typically having about 20-500 alkylene oxide units. The alcohols R-OH can also have been alkoxyated with THF.

20 In general, the compound (iii) is used with regard to the free isocyanate groups in an at least stoichiometric amount, but frequently in stoichiometric excess, for example from 50% to 100%, based on free NCO groups.

25 The hydrophobic group R can also be attached to the polyetherdiol (ii) via an ester or ether bridge. Associative thickeners of the general formula (II) are thus obtainable by reaction of

- (i) polyetherdiols with
 (iv) compounds of the general formula R-OH or R-COOH, where R is a hydrophobic
 30 aliphatic or aromatic radical of at least 4 carbon atoms and has the above-mentioned meanings, wherein R-OH may have been alkoxyated (as described above), and also further derivatives thereof that are capable of forming an ether or ester bond.

Compounds of the formula (III) are finally obtained from the diisocyanates (ii) and the compounds (iii) without polyetherdiols (i) being present. The compounds (iii) can be used in stoichiometric excess.

- 5 In a particularly preferred embodiment, the aqueous pretreatment liquors according to the present invention comprise polymers or copolymers of diallyldialkylammonium monomers and especially diallyldimethylammonium chloride homopolymer as polycationic compounds (A) and one or more associative thickeners of the formula (I) and/or (II) as thickeners (B).

10 As well as the components (A) and (B), the aqueous treatment liquors according to the present invention may comprise customary additives as a component (C). Examples of customary additives are defoamers, emulsifiers, solvents, biocides, deaerators and wetting agents.

- 15 The aqueous treatment liquors according to the present invention typically comprise
- (a) from 0.1% to 50% by weight and preferably from about 0.5% to 30% by weight of the polycationic compounds (A),
 - (b) from 0.1% to 50% by weight and preferably from 0.5% to 30% by weight of the thickeners (B),
 - 20 (c) from 0% to 30% by weight and preferably from 0.5% to 20% by weight of customary additives (C), and
 - (d) water ad 100% by weight.

- 25 What is surprising is particularly that the pretreatment liquors according to the present invention provide – in one and the same liquor – distinct improvements both in the properties of cotton fabrics and those of polyester fabrics for printing with pigment inks and with disperse dye inks, respectively. Cotton or cotton blend fabrics are typically printed with pigment inks and polyester fabrics typically with disperse dye inks. In
- 30 addition, the pretreatment has a favorable effect on fixation when printing with disperse dye inks, permitting more brilliant as well as darker (especially black) colors.

It is a further surprise that the hand of the substrates pretreated according to the present invention is not adversely affected.

The present invention further provides a treatment composition comprising the components (A), (B) or optionally (C) whence the aqueous treatment liquors according to the present invention are obtainable by diluting with water.

- 5 A further aspect of the present invention is a process for printing sheetlike textile substrates by the inkjet process, characterized by the textile substrates to be printed being pretreated with the aqueous pretreatment liquors.

The present invention further provides the printed textile substrates themselves.

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The present invention yet further provides a process for pretreating textile substrates with the aqueous pretreatment liquors according to the present invention.

- 15 The pretreatment operation for inkjet printing comprises applying the pretreatment liquor and subsequently drying the impregnated textile substrate.

The pretreatment liquor can be applied by an exhaust process or by a continuous process involving a forced application.

- 20 Exhaust processes are suitable whenever the pretreatment agent possesses distinct affinity for the substrate. This will be particularly the case when the pretreatment agent and the substrate possess different ionogenicities, for example in that the pretreatment agent is cationic in nature and the substrate fiber anionic. There are various forms of the exhaust process which are known in principle from the field of dyeing. For example, the textile can
25 be in a wound-up state. The treatment liquor is then forced under pressure through the wound-up textile, and the direction of flow of the treatment liquor can be from in to out or else, in fully flooded machines, from out to in. To ensure a uniform application, a change in the direction of flow of the treatment liquor is advantageous. In another embodiment, the fabric is in an unconstrained state in the pretreatment liquor and moves with the
30 pretreatment liquor. In a further embodiment, the textile can also be pulled through a standing bath. In this case, the textile is preferably repeatedly pulled through the treatment bath. The direction of movement of the textile should reverse, since this is conducive of a uniform application. More particular details concerning these application processes can be found in the relevant literature, for example Veredlung von Textilien, VEB
35 Fachbuchverlag Leipzig, 1st edition 1976, page 93 ff.

Useful continuous processes for application include all processes in which the pretreatment composition according to the present invention can be applied uniformly or imagewise. Of particular suitability here are all printing processes and also all processes in which the textile is uniformly saturated with the pretreatment composition. The fundamental difference from the exhaust processes is that a forced application is realized. The pretreatment liquor need not have any affinity for fiber for these processes.

Useful printing processes include for example all screen printing processes. Screen printing is an important process which is utilized inter alia in the production of printed fabrics. In screen printing, the print pastes are forced by a squeegee through a fine mesh and onto the substrate to be printed. The mesh can be formed from synthetic fibers, as in flat screen printing machines, or metals, as in rotary screen printing machines.

But relief printing, gravure printing or roller printing, being common textile printing processes, are also suitable for applying the pretreatment liquor. More particular details concerning the individual printing processes can be found on pages 110 ff of the literature reference cited above.

As well as printing processes, however, it is also possible to use any technique wherein the textile is uniformly saturated with the pretreatment liquor. This is accomplished for example in the form that the textile is led through a trough filled with the pretreatment composition and subsequently squeezed off by two rollers to a defined wet pickup. But the application can also be accomplished in the form that the textile is led through a nip formed between two rotating rollers and filled with the pretreatment liquor. The rollers will simultaneously squeeze off the textile material to the desired wet pickup. There are in addition many other possible configurations for this pad-mangle technology, which are all likewise suitable for applying the pretreatment liquor.

In addition, defined amounts of the pretreatment liquor can be applied by generally known spraying and pouring techniques.

After the pretreatment composition has been applied, the textile is dried. This may be accomplished by heating the impregnated textile sufficiently for the water present to be able to evaporate off. It is preferable to employ temperatures of 80 and 120°C. The heat needed can be introduced in the form of heated air as a heat transfer agent. But it is also

possible to use infrared radiators or microwave radiators. Preferably, the textile is kept under tension in this operation in order that the formation of creases may be avoided.

Examples of textile substrates to be printed which are pretreated according to the present invention are fibers, yarns, threads, knits, wovens, nonwovens and garments composed of polyester, modified polyester, polyester blend fabric, cellulosic materials such as cotton, cotton blend fabrics, jute, flax, hemp and ramie, viscose, wool, silk, polyamide, polyamide blend fabrics, polyacrylonitrile, triacetate, acetate, polycarbonate, polypropylene, polyvinyl chloride, polyester microfibers and glass fiber fabrics.

The inkjet process typically utilizes aqueous inks, which are sprayed as small droplets directly onto the substrate. There is a continuous form of the process, in which the ink is pressed at uniform rate through a nozzle and the jet is directed onto the substrate by an electric field depending on the pattern to be printed, and there is an interrupted inkjet or drop-on-demand process, in which the ink is exposed only where a colored dot is to appear, the latter form of the process employing either a piezoelectric crystal or a heated hollow needle (bubble jet process) to exert pressure on the ink system and so eject an ink droplet. These techniques are described in Text. Chem. Color, volume 19 (8), pages 23 to 29, 1987, and volume 21 (6), pages 27 to 32, 1989.

The inkjet inks used for printing textile substrates in the process according to the present invention, as well as dispersants, typically contain water or a water-solvent mixture and also finely divided organic or inorganic colorants which are preferably substantially insoluble in water or in the water-solvent mixture, these colorants being, for example by the definition in German standard specification DIN 55944, pigments. Disperse dyes can be used instead of pigments. But the inks can also contain direct, acid, reactive and vat dyes as dissolved dyes. The soluble dyes mentioned can be present as brightening agents in pigment preparations, in which case the soluble dyes used, especially direct, acid or reactive dyes, are similar in hue to the pigment.

The example which follows illustrates the invention.

Example

A Making a pretreatment liquor

Component A: associative thickener, reaction product of HDI with ethoxylated fatty alcohol having a molecular weight of about 10 000 g/mol, the ethoxylated fatty alcohol having been used in an excess of 50%, based on isocyanate groups;

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component B: diallyldimethylammonium chloride homopolymer as a polycationic compound;

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for 1 kg of liquor 889.8 g of demineralized water are stirred with 10 g of component A until everything has dissolved. This is followed by stirred addition of 100 g of component B and 0.2 g of a commercially available defoamer (Entschäumer TC from BASF AG) and homogenization.

B Pretreatment of a textile fabric

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The following fabrics were pretreated by padding with the pretreatment liquor:

- (1) cotton 283
- (2) polyester flagging
- (3) 50/50 cotton/polyester blend fabric

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The liquor is filled into the padder. The fabric is led through the liquor in the padder and then squeezed off between 2 rolls.

The fabric is then dried at 80°C.

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C Printing the pretreated fabric with a pattern

- a) The cotton fabric (1) and the cotton/polyester blend fabric (3) are printed with a pigment ink (Helizarin® ink) on a Mimaki TX 1600 S printer.
- b) The polyester fabric (2) is printed with a disperse dye ink (Bafixan® ink) on an Epson 3000 printer.

30

The ink add-on is the range from 100% to 400%.

- 35 The printed polyester fabric (2) is subsequently fixed with hot air for about 90 s.

D Reduction clearing the prints

The prints are subsequently reduction cleared by

- (i) rinsing in cold water, followed by hot water,
- 5 (ii) subsequent treatment at 80°C in a mixture of 2g/L of concentrated hydrosulfite solution, 2mL/L of 50% by weight aqueous sodium hydroxide solution, 1mL/L of Kieralon DB and 2mL/L of Trilon TA for 10-12 min,
- (iii) followed by a cold rinse for 2-3min,
- (iv) neutralization in a solution of 1mL/L of glacial acetic acid,
- 10 (v) a further cold rinse.

E Quantitative examinations by colorimetry

- Quantitative examinations were carried out by means of colorimetry. The measurements
 15 were carried out using an X-Rite CA22 spectrophotometer and analyzed using X-Rite Color Master software.

- The respectively untreated fabric was used as a standard for the colorimetric measurements. A higher value for color strength and for chroma (as per M. Richter, Einführung in die Farbmeterik, DeGruyter, Berlin 1981) for the textile pretreated according
 20 to the present invention thus is evidence of an improved print result.

- I. Helizarin® on cotton 283, fabric weight = 119.7 g/m², cotton poplin, staple length 25-30 mm, Tegewa degree of desizing 9, average degree of polymerization >1800;
 25 standard: untreated fabric. The results are summarized in table 1.

Table 1

| Color | Color strength untreated | Color strength pretreated | Δ chroma |
|---------|--------------------------|---------------------------|----------|
| cyan | 100 | 150.84 | 5.71 |
| magenta | 100 | 124.97 | 1.55 |
| yellow | 100 | 132.89 | 4.49 |
| black | 100 | 220.2 | -0.15 |

- II. Helizarin® on cotton/polyester blend fabric (50% cotton), fabric weight =
 30 114.7g/m². The results are summarized in table 2.

Table 2

| Color | Color strength untreated | Color strength pretreated | Δ chroma |
|---------|-----------------------------|------------------------------|-----------------|
| cyan | 100 | 197.38 | 4.81 |
| magenta | 100 | 119.64 | 1.10 |
| yellow | 100 | 147.48 | 6.58 |
| black | 100 | 219.14 | 0.92 |

- 5 III. Bafixan® on polyester flagging, fabric weight = 104.7 g/m². The results are summarized in table 3.

Table 3

| Color | Color strength untreated | Color strength pretreated | Δ chroma |
|---------|-----------------------------|------------------------------|-----------------|
| cyan | 100 | 212.51 | 0.60 |
| magenta | 100 | 130.65 | 1.01 |
| yellow | 100 | 187.92 | 9.16 |
| black | 100 | 115.40 | -0.92 |

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Qualitative comparison:

The pretreatment of the fabric has improved ink holdout, giving better resolution. Fabric hand is not impaired by the pretreatment.

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